

# Electronic structure of graphite fluorides

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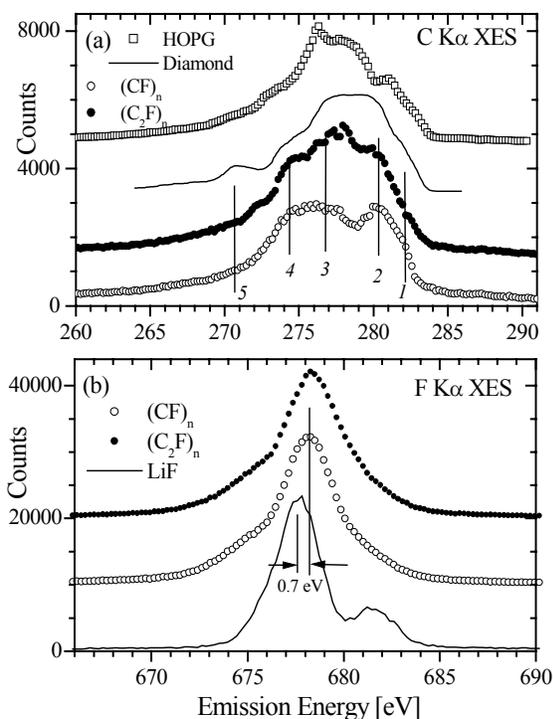
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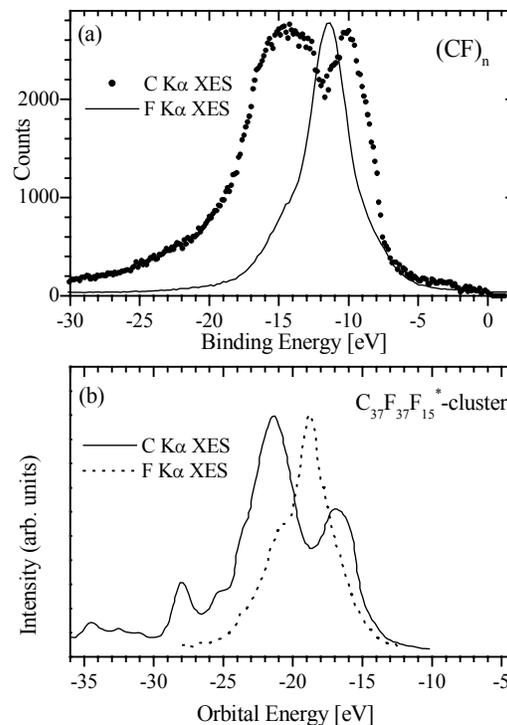
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Fluorination of graphite leads to the formation of polycarbon monofluoride (CF)<sub>n</sub> and polydicarbon monofluoride (C<sub>2</sub>F)<sub>n</sub>. These compounds are exceptional lubricants under high temperature and high vacuum and quite successful cathodic depolarizers in a high-energy density battery. It is supposed that their structure is layered and altered from graphite by inserting covalently bonded fluorine atoms above and below every hexagon in each layer. According to Ref. 1 the structure of graphite fluorides is an infinite array of *trans*-linked cyclohexane chairs. It also has been suggested that it might be an infinite array of *cis-trans*-linked cyclohexane boats [2]. First principle calculations of the stability of these two configurations have shown that the energetic difference between these two structures is 0.0725 eV/atom in favour of the chair conformation, which is considered now the optimal structure for graphite fluorides [3]. Based on these recently performed *ab-initio* band structure calculations for (CF)<sub>n</sub> it has been concluded that carbon atoms have completely lost their aromatic nature [3]. In order to experimentally verify these conclusions regarding the chemical bonding, we have measured carbon and graphite X-ray emission spectra (XES) of (CF)<sub>n</sub> and (C<sub>2</sub>F)<sub>n</sub>.

The measurements were performed at Beamline 8.0 using the soft X-ray fluorescence endstation [4]. The samples were excited non-resonantly at 310 eV and 720 eV. Fig. 1 a shows X-ray fluorescence measurements of (CF)<sub>n</sub> and (C<sub>2</sub>F)<sub>n</sub> [5]. Carbon K $\alpha$  XES of (CF)<sub>n</sub> and (C<sub>2</sub>F)<sub>n</sub> display features labelled 1-5 that are more similar to those of diamond where carbon atom has *sp*<sup>3</sup> bonding configuration than to graphite (configuration *sp*<sup>2</sup>). Our findings confirm that in (CF)<sub>n</sub> and (C<sub>2</sub>F)<sub>n</sub> all carbon atoms are of *sp*<sup>3</sup> type and covalently bonding to fluorine. This is in good agreement with results of nuclear magnetic measurements [6] according to which a resonance line is observed in the <sup>13</sup>C NMR spectrum of graphite fluoride and attributed to the *sp*<sup>3</sup> carbon atoms. Fig. 1 b presents fluorine K $\alpha$  emission measurements of (CF)<sub>n</sub> and (C<sub>2</sub>F)<sub>n</sub>. A chemical shift in the F K $\alpha$  emission spectra of about 0.7 eV takes place with respect to the spectrum of the ionic compound LiF. On the other hand, an increase in line width is observed for F K $\alpha$  XES of (CF)<sub>n</sub> (~3.1 eV) and (C<sub>2</sub>F)<sub>n</sub> (~3.6 eV) with respect to that of LiF (~2.8 eV). Both effects could be due to an increase in covalency in the chemical bonding. The fluorine spectra therefore also show that fluorine atoms are covalently bonding to carbon atoms.



**Fig. 1 Carbon (a) and fluorine (b) XES of  $(CF)_n$ ,  $(C_2F)_n$  and reference compounds.**



**Fig. 2 (a) Experimental carbon and fluorine K $\alpha$  XES of  $(CF)_n$ . (b) Theoretical C and F K $\alpha$  XES of  $C_{37}F_{37}F_{15}^*$ -cluster.**

Fig. 2 shows carbon and fluorine spectra of  $(CF)_n$  in the binding energy scale. The emission energies are converted to binding energies using XPS C 1s and F 1s measurements of  $(CF)_n$  [ $E_{b.e.}(C\ 1s) = 290.4\ eV$  and  $E_{b.e.}(F\ 1s) = 689.6\ eV$ ]. These emission spectra are caused by  $2p \rightarrow 1s$  dipole transitions and therefore give a possibility to study the occupied carbon and fluorine 2p-states. Both spectra show a negligible intensity in the vicinity of the Fermi level, which is in agreement with electrical measurements of  $(CF)_n$  according to which this material is an insulator. The intensity maximum of fluorine K $\alpha$  XES occupy some intermediate position between two main peaks of carbon K $\alpha$  XES of  $(CF)_n$ . According to the band structure calculations [3], F 2p-states are located at the bottom of the valence band: the F  $\sigma$  band is separated from the bottom of the C  $\sigma$  band by a gap of 8.4 eV at  $\Gamma$  and the F  $\pi$ -bands span a 6.8 eV range below the Fermi level interacting with lower  $\pi$  and upper  $\sigma$  carbon bands. The experiment shows (see Fig. 2) that F 2p-states are located at the middle of the valence band pushing up and down the carbon 2p-subbands. Our findings are more close to results of semi-empirical MO LCAO calculation of electronic structure of  $(CF)_n$  [7]. According to these MO LCAO calculations, carbon 2p-states form two subbands originating from  $\sigma(C-C)$ ,  $\tau^*(C-F)$  and  $\sigma(C-C)$ ,  $\tau(C-F)$  orbitals, respectively, divided by  $\sim 4.7\ eV$  (Fig. 2b). Fluorine 2p-states are formed by the F 2p lone pair and occupy energy range between carbon 2p-subbands (Fig. 2b). The tails of fluorine 2p-states overlap with carbon 2p-states forming  $\tau^*(C-F)$  and  $\tau(C-F)$  bonds. This MO LCAO structure is in an agreement with carbon and fluorine K $\alpha$  XES (see Fig. 2a). The splitting of C K $\alpha$  XES of  $(CF)_n$  is found to be about 4.6 eV and F K $\alpha$  XES is located exactly in minimum between two peaks of carbon spectrum.

To conclude, we have studied X-ray emission spectra of constituents of  $(CF)_n$  and  $(C_2F)_n$ . We found that carbon atoms are of the  $sp^3$  type and covalently bound to fluorine. Our measurements show that results of band structure calculations based on chair-type structure of  $(CF)_n$  are not confirmed. Therefore the crystal structure of graphite fluorides is still not solved and must be refined.

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